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Thermodynamics of 2- and 3-cyanopyridine from vibrational spectra

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Abstract : The various thermodynamic functions, namely, the heat capacity, the enthalpy, the entropy and free energy of 2- and 3-cyanopyridine have been computed in the temperature range 200–1500 K by using the standard expressions at 1 atmospheric pressure under the rigid rotator harmonic oscillator approximation.

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The energy of a molecule consists partly of translational, rotational, vibrational and electronic energies. To a first approximation, contributions of these energies can be treated separately. Once the vibrational frequencies of a molecule are known, it is possible to calculate the contribution of the vibrational energy to the total energy possessed by a molecule. The rotational energy contribution can be calculated if the moments of inertia of the molecule are known. The thermodynamic functions of 4-cyariopyndine were reported by Medhi and Sarma [1]. The Raman and IR spectra of 2- and 3-cyanopyridine were recorded [Figures not shown]. The vibrational analysis of 2- and 3-cyanopyndme as reported by Isaq *et al* [2] have been utilized to calculate the thermodynamic functions in ideal gas state for the said cyanopyridine molecules at 1 atmosphere pressure under the usual approximation of rigid rotator, harmonic oscillator model in the temperature range 200–1500 K. Since the thermodynamic functions of these molecules are not yet reported so the decision to compute and report them was taken into consideration by using IBM-PC/AT computer.

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The moment the vibrational frequencies of a molecule are obtained from the vibrational spectra, it is possible to compute with great precision, the values of the various thermodynamic functions. The spectroscopically measured frequencies and the moment of inertia are important variables in determining these functions of a molecule. Such calculations provide the unique method to obtained these data particularly because the direct experimental measurement of these quantities is usually tedious and even may not be reliable.

The total partition function (Q) can be expressed as the product of the individual partition functions due to translational, rotational, vibrational and electronic energies. Hence

$$Q = Q_{trans} \cdot Q_{rot} \cdot Q_{vib} \cdot Q_{elec} \quad (1)$$

$$= \Sigma g_i \exp(-\epsilon_i/kT), \quad (2)$$

where g_i is the statistical weight of the i-th energy level [3], k is the Boltzmann constant and T is the temperature in Kelvin. In terms of partition function, the total energy E^0 of one mole of an ideal gas, is given by

$$E^0 = E^0_0 + RT^2\, d \ln Q/dT,$$

where

E^0_0 = Energy at zero kelvin,

R = Gas constant, and

T = Absolute temperature.

Using the above, the various thermodynamic functions are given as

Enthalpy function $(H^0 - E^0_0)/T$

$$= RT\, d/dT\ (\ln Q) + R, \quad (4)$$

Heat capacity $(C^0_p) = d/dT[RT^2\, d/dT(\ln Q)] + R, \quad (5)$

Free energy function $(G^0 - E^0_0)/T = -R \ln Q/N, \quad (6)$

Entropy function $(S^0) = -RT\, d/dT\ (\ln Q) + R \ln Q$

$$- R \ln N + R. \quad (7)$$

In order to get the total value of a thermodynamic function, the contributions to these functions from different types of partition functions are added. The electronic contribution is small and hence ignored as ϵ_{elec} is large enough in comparision to kT at ordinary temperature.

Hence, ignoring the elctronic contribution, the translational rotational and vibrational contributions are given as under

$$\left(H^0 - E^0_0\right)/T = R[4 + \sum^{3N-6} \{\chi_i / \exp \chi_i - 1\}] \quad (8)$$

$$C^0_P = R[4 + \sum_{i=1}^{3N-6} \{\chi_i^2 \exp \chi_i /(\exp \chi_i - 1)^2\}] \quad (9)$$

$$(G^0_0 - E^0_0)/T = -R \ln Q/N$$

$$= -R[3/2 \ln M + 4 \ln T + 1/2 \ln(I_A I_B I_C) - \ln \sigma_0$$

$$+ \sum^{3N-6} \ln[1 - \exp \upsilon_i hc/kT], \quad (10)$$

$$S^0 = (H^0 - E^0_0)/T - (G^0 - E^0_0)/T, \quad (11)$$

where $\chi_i = hc\upsilon_i/kT$,

σ_0 = symmetry number of overall rotation of the molecule,

υ_i = fundamental frequency in terms of wave number,

I_A, I_B and I_C are principal moments of inertia.

The stastical mechanical calculations of thermodynamic properties for 2-cyanopyridine and 3-cyanopyridine molecules requires atomic masses, molecular weights, molecular structural parameters, complete fundamental vibrational frequencies ($3N$–6) and the symmetry number. The atomic masses used in calculations were taken from literature [1,4–7] and given as : C, (12.01115); H, (1.00797); N, (14.0067).

The two cyanoderivatives of pyridine molecule under consideration hav been considered to have C_{2v} symmetry with their external symmetry number equal to 3 and internal rotation as 2. In the computation of principal moment of inertia I_x, I_y and I_z, all the molecules have been considered as planar and the Z-axis perpendicular to the plane. The principal moment of inertia were found to be 130.89, 642.67 and 773.57 × 10^{39} g cm^2 in 2-cyanopyridine and 129.32, 614.61 and 743.93 × 10^{-39} g cm^2 in 3-cyanopyridine respectively.

For determining rotational contributions for the title molecules, the following structural parameters were used [4, 8–11].

Bond length (A)	Bond angle (°)
2-cyanopyridine	
$N_1 - C_2 = 1.41$, $C_2 - C_3 = 1.40$	$N_1C_2C_3 = 120$, $C_2C_3C_4 = 122$
$C_3 - C_4 = 1.39$, $C_4 - C_5 = 1.39$	$C_3C_4C_5 = 120$, $C_4C_5C_6 = 120$
$C_5 - C_6 = 1.39$, $C_6 - N_1 = 1.40$	$C_5C_6N_1 = 118$, $C_6N_1C_2 = 120$
$C_3 - C_7 = 1.37$, $C_7 - N_8 = 1.20$	$C_2C_3C_7 = 119$, $C_4C_3C_7 = 119$
	$C_3C_7N_8 = 180$
3-cynopyridine	
$N_1 - C_2 = 1.41$, $C_2 - C_3 = 1.40$	$N_1C_2C_3 = 122$, $C_2C_3C_4 = 120$
$C_3 - C_4 = 1.39$, $C_4 - C_5 = 1.39$	$C_3C_4C_5 = 120$, $C_4C_5C_6 = 120$
$C_5 - C_6 = 1.39$, $C_6 - N_1 = 1.40$	$C_5C_6N_1 = 119$, $N_3C_2C_7 = 119$
$C_3 - C_7 = 1.37$, $C_7 - N_8 = 1.20$	$N_1C_2C_7 = 119$, $C_6N_1C_2 = 119$
	$C_2C_7N_8 = 180$

Here, C_2 to C_5 are carbon atoms of the ring and C_7 is the carbon of the -CN group, N_1 and N_8 represents the nitrogen of the ring and -CN group respectively.

The computed results of the thermodynamic functions, namely, the heat capacity at constant pressure (^0C_p), the enthalpy function $(H^0 - E^0_0)/T$, the free energy function $[-(G^0 - E^0_0)/T]$ and the entropy (S^0) for the said molecules

Table 1. Thermodynamic function (cal K^{-1} mol^{-1}) of 2-cyanopyridine.

Temp. (K)	$(H^0-E^0_0)/T$	C_p^0	$-(F^0-E^0_0)/T$	S^0
200	10.6467	14.2421	54.54267	65.139
300	12.5973	18.8285	57.37099	69.96833
400	14.7292	23.3391	59.38653	74.11571
500	16.8487	27.1865	60.95973	77.80848
600	18.839	30.272	62.55321	81.09318
700	20.6522	32.691	64.35332	84.0055
800	22.2799	34.5796	65.5115	86.59141
900	23.7321	36.0607	66.96086	88.89296
1000	25.0258	37.2323	68.02405	90.94982
1100	26.1796	38.1685	69.21722	92.94982
1200	27.2112	38.9248	70.65233	94.64358
1300	28.1368	39.5422	71.8385	95.97532
1400	28.9702	40.0513	72.68283	97.35307
1500	29.7235	40.4752	73.39096	98.61448

H^0 = enthaply; C_p^0 = heat capacity; S^0 = entropy; F^0 = free energy; and E^0_0 = zero point energy.

Table 2. Thermodynamic function (cal K^{-1} mol^{-1}) of 3-cyanopyridine.

Temp. (K)	$(H^0-E^0_0)/T$	C_p^0	$-(F^0-E^0_0)/T$	S^0
200	11.4132	16.5655	54.63488	66.04812
300	14.0073	21.6879	57.47039	71.47773
400	16.4752	25.9214	59.49659	75.97177
500	18.7174	29.3217	61.07878	79.79616
600	20.7187	32.0095	62.67947	83.09724
700	22.4874	34.114	64.68535	85.97272
800	24.0477	35.7592	66.14814	88.49586
900	25.4236	37.0511	67.30126	90.72487
1000	26.6394	38.0735	68.66753	92.70696
1100	27.7174	38.8905	70.26328	94.48066
1200	28.6769	39.5503	71.01057	96.07749
1300	29.5347	40.0887	71.9886	97.52333
1400	30.0349	40.5342	72.53454	98.83946
1500	30.9994	40.9016	73.04406	100.0435

H^0 = enthaply; C_p^0 = heat capacity; S^0 = entropy; F^0 = free energy; and E^0_0 = zero point energy.

in the temperature range 200-1500 K are represented in Tables 1 and 2. The observed frequencies and their intensities with assignments of these molecules are given in Table 3.

Table 3. Assignments of vibrational frequencies of 2-cyanopyridine and 3-cyanopyridine (all values in cm^{-1}).

2-Cyanopyridine		3-Cyanopyridine		Assignments
IR	Raman	IR	Raman	
3438 m	–	3439 mb	–	–
–	3098 w	–	3080 s	νCH
3061	3067 ms	3069 s	3061 s	νCH
3010 vw	–	3005 vvw	–	νCH
2238 vs	2237 vs	2229 vs	2232 vs	νCN
1584 vvs	1585 vs	1586 vs	1588 s	νCC
1529vvw	–	1563 vs	–	νCC
1463 vs	–	1471 vs	1474 vw	νCC, CN
1433 vs	1433 vvw	1418 vs	1422 vw	νCC, CN
1291 ms	1298 vvw	1244 vvw	1290 vvw	βCH
1250 ms	1253 w	1210 ms	1241 vvw	νCC
1155 ms	1155 ms	1185 ms	1189 ms	βCH
1092 ms	1062 vvw	1080 vvw	1062 vvw	βCH
1045 ms	1045 m	–	1035 s	βCH
993 vs	992 vs	1023 s	1023 ms	ν ring
910 w	–	927 w	–	γCH
782 vvs	779 ms	810 vs	780 m	γCH
632 m	634 vw	630 vs	630 w	βCC
554 vvs	552 vw	554 vs	554 w	βCC
470 m	–	471 s	473 m	βCC
402 vvs	403 vvw	403 s	400 vvw	γCC
–	362 w	–	358 w	βCN
–	176 ms	–	176 s	γCN
–	161 ms	–	160 ms	lattice vibration

ν - stretching β - in plane bending γ - out of plane bending

vvs - very very strong vs - very strong s - strong

ms - medium strong m - medium mb - medium broad

vvw - very very weak vw - very weak w - weak

sh - shoulder

The thermodynamic functions rises more rapidly in the low temperature range and less rapidly in the high temperature range. The variation of the thermodynamic functions with temperature is represented in Figures 1 and 2. The values of the entropy and other functions do not differ appreciably for the two molecules which show that the change in position of -CN group does not bring much change in their thermodynamic functions. Similar trend is reflected from the observed fundamentals [2]. The variations

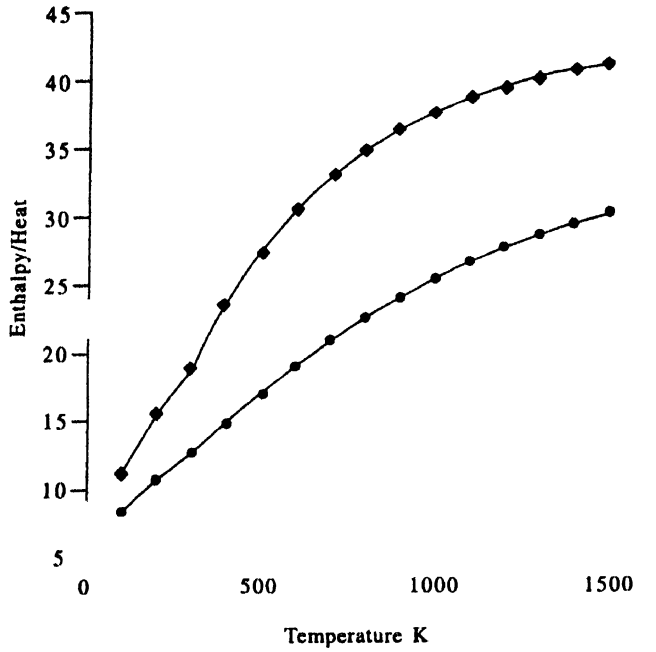

Figure 1. Variation of enthalpy (•)/heat capacity (♦) with temperature for 2-cyanopyridine.

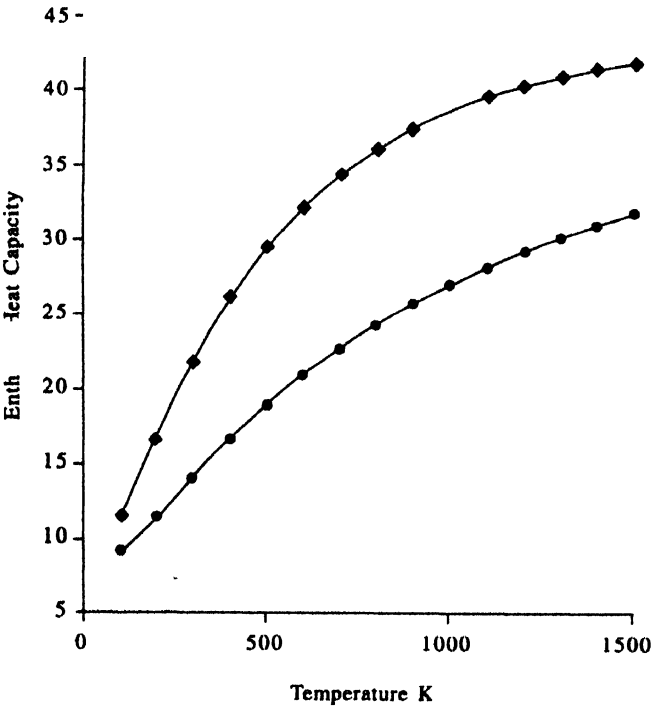

Figure 2. Variation of enthalpy (•) / heat capacity (♦) with temperature for 3-cyanopyridine.

of these thermodynamic functions with temperature are in agreement with trend reported in the literature [6,12–15].

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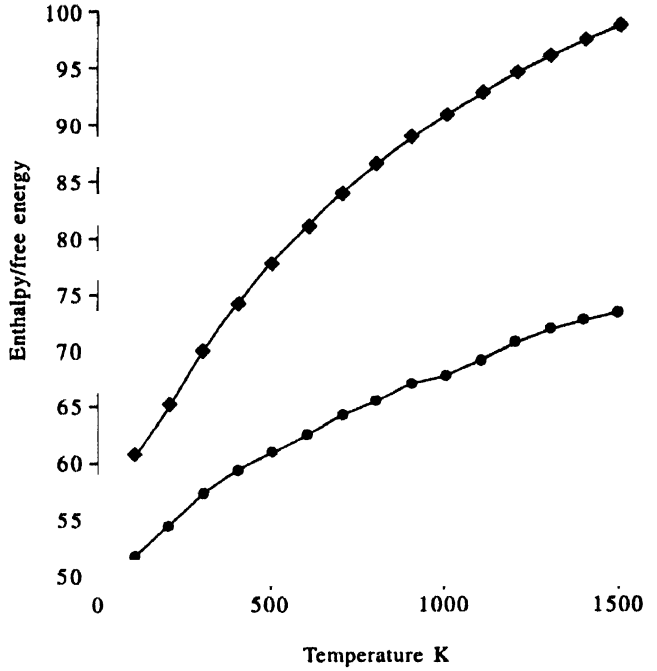

Figure 3. Variation of entropy (♦)/free energy (•) with temperature for 2-cyanopyridine.

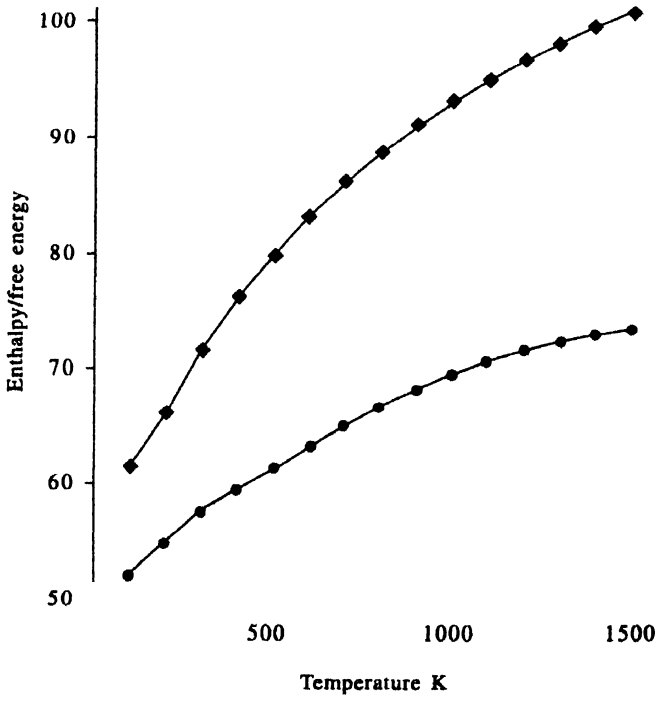

Figure 4. Variation of entropy (♦)/free energy (•) with temperature for 3-cyanopyridine.

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